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(54) Title: METHODS FOR PATTERNING POLYMER FILMS, AND USE OF THE METHODS

(54) Titre: PROCEDES PERMETTANT DE FAÇONNER DES FILMS POLYMERES ET UTILISATION DE CES PROCEDES

(57) Abstract

In a method for patterning a polymer film forming a coating on a material surface, a thin film of polymer is deposited on the surface and the patterning takes place by applying to the material surface a stamp made of an elastomeric material in conformal contact with the surface of the thin film, such that portions thereof contacting one or more protruding elements of the elastomeric stamp formed by one or more indentations thereof, are attached to the protruding element or elements and removed from the material surface with the stamp. In a method for transferring a patterned polymer film onto a material surface, a thin film polymer is deposited on a stamp surface and the stamp is applied in conformal contact with the material surface, such that thin film of polymer is transferred thereto from one or more protruding elements of the elastomeric stamp formed by at least one indentation thereof, thus leaving a patterned thin film of polymer on the material surface when removing the stamp therefrom. Use for patterning an etched resist in the form of a thin film of polymer on a gold layer.

(57) Abrégé

Dans un procédé utilisé pour façonner un film polymère formant un revêtement sur une surface de matériau, on dépose un mince film de polymère sur la surface et on imprime des motifs en appliquant sur la surface du matériau, un tampon en matière élastomère en contact intime avec la surface du film mince de sorte que des parties de ce dernier qui se trouvent en contact avec un ou plusieurs éléments saillants du tampon élastomère formés par un ou plusieurs renforcements, soient attachés à l'élément ou aux éléments saillants et enlevés de la surface du matériau avec le tampon. Dans un procédé permettant de transférer un film polymère façonné sur une surface de matériau, on dépose un mince film de polymère sur une surface de tampon puis on applique le tampon en contact intime avec la surface de matériau pour que le mince film de polymère soit transféré sur la surface par un ou plusieurs éléments saillants du tampon élastomère formés par au moins un renforcement, ceci laissant un film mince façonné de polymère sur la surface du matériau lorsqu'on enlève le tampon. On peut utiliser ce procédé pour façonner une épargne gravée sous forme d'un mince film de polymère sur une couche d'or.

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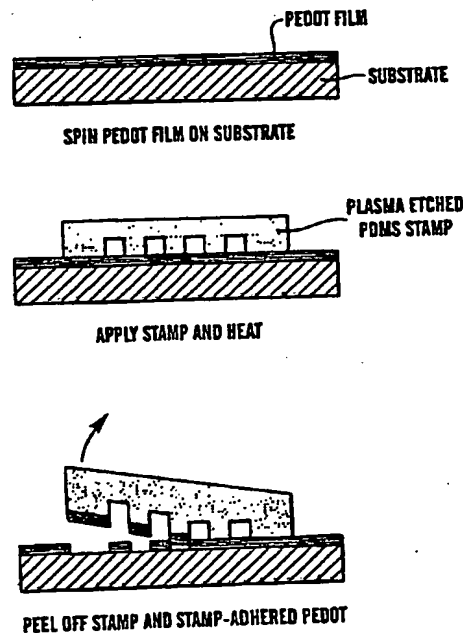
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(54) Title: METHODS FOR PATTERNING POLYMER FILMS, AND USE OF THE METHODS

(57) Abstract

In a method for patterning a polymer film forming a coating on a material surface, a thin film of polymer is deposited on the surface and the patterning takes place by applying to the material surface a stamp made of an elastomeric material in conformal contact with the surface of the thin film, such that portions thereof contacting one or more protruding elements of the elastomeric stamp formed by one or more indentations thereof, are attached to the protruding element or elements and removed from the material surface with the stamp. In a method for transferring a patterned polymer film onto a material surface, a thin film polymer is deposited on a stamp surface and the stamp is applied in conformal contact with the material surface, such that thin film of polymer is transferred thereto from one or more protruding elements of the elastomeric stamp formed by at least one indentation thereof, thus leaving a patterned thin film of polymer on the material surface when removing the stamp therefrom. Use for patterning an etched resist in the form of a thin film of polymer on a gold layer.



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Description

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Methods for patterning polymer films, and use of the methods

The present invention concerns a method for patterning a polymer film forming a coating on a material surface, wherein the patterning takes place by means of a stamp having a surface with at least one indentation formed therein, and a method for transferring a patterned polymer film onto a material surface by means of a stamp having a surface with at least one indentation formed therein. The invention also concerns the use of methods of this kind.

The use of conjugated polymers in electronic devices requires means for processing them into patternable thin films. Patterning conducting electrodes and semiconducting polymers in polymer diodes requires patterning of all materials, at a resolution of 0.1-50 μm . This can possibly be accomplished by the use of classical photolithography with help of photoresists, but several new problems arise in the chemical etching of the material and the chemical compatibility with conventional photoresists. It would therefore be desirable to pattern this material with non-photolithographic techniques.

A new method for patterning is based on elastomeric stamps. Patterning of a surface here requires conformal contact between the stamp and surface. Many variants of these techniques are documented, in particular in the work from G. Whitesides' group at Harvard University (Y. Xia and G. Whitesides, *Soft lithography*, *Angewandte Chemie-International Edition in English* 37(5): 551-575 (1998) and Y. Xia and G. Whitesides, *Soft lithography*, *Annual Review of Materials Science*, 28:153-184 (1998)).

The work of Whitesides' group is disclosed in US patent No. 5 512 131, titled "Formation of microstamped patterns on surfaces and derivative articles" (Kumar & Whitesides). This prior art document discloses a method of patterning a material surface, comprising steps of providing a stamp having a surface including at least one indentation formed therein, said indentation configured with a stamping surface defining a first pattern; coating said stamping surface with a molecular species terminating at the first end in a functional group selected to bind to said material; processing said stamping surface in a first orientation and contacting a portion of said material surface with said stamping surface to hold said molecular species against said material surface portion to allow said functional group to bind thereto; and removing said stamping surface to provide a self-assembled

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5 molecular species on said material surface according to said first pattern in said first orientation.

10 This prior art disclosure amounts to a process wherein a chemical species capable of forming a self-assembled monolayer is coated onto the stamping
5 surface of an elastomeric stamp, said species having a functional group selected to bind to a particular material. The stamping surface is placed against a surface of a material surface and removed to leave a self-assembled
15 monolayer of the species according to the stamping surface pattern of the stamp.

10 Further there is known a number of different prior art techniques for patterning surfaces or materials deposited thereon without having to resort to conventional photolithography.

20 As a further example of prior art a paper by Zhang, L.G.; Liu, J.F. and Lu, Z.H., titled "Microfabrication on polymer with a contact procedure",
25 15 Supramolecular Science, Vol. 5, Nos. 5-6:713-715 (Oct-Dec. 1998) discloses the fabrication of thickness-contrast micropatterns based on a contact procedure. Polymer (polydimethylsiloxane) micropost arrays are fabricated with grids as the masters. This contact procedure, which does not rely on
30 etching, extends the present limits of microfabrication. In addition the thickness-contrast micropatterns on the polymer can be replicated to other
20 substrates, such as silicon wafers, with microcontact printing.

35 These techniques that are collected in the catchall term soft lithography are based on pattern transfer by a soft rubber stamp in direct contact with the surfaces and materials to be patterned. Soft lithography includes
25 microcontact printing (μ CP), replica molding (REM) and micromolding in capillaries (MIMIC). The patterning technique is based on physical contact, not the projection of light through a mask, as in photolithography. The
40 fundamental limits to resolution are due to the range of the van der Waals forces determining the interaction of surfaces (~ 10 nm), not the diffraction of
30 light in far-field geometries (~ 0.5 μ m).

45 An important element of microcontact printing (μ CP) is the formation, by selfassembly, of a monomolecular layer of etch resistant organic molecules. Alkanethiols are the preferred species, which chemisorb into molecular thin
50 films on Au, Ag, Cu and other metal surfaces. They form layers of very small

5 thickness (1-3 nm) which are tightly bound (but can be desorbed at high
temperatures and by exchange). These alkane layers are used as the resist; a
10 metal layer is protected from etching below the molecular film, and where it
is not deposited the metal is removed. The patterning of the resist layer is in
5 its turn done with molecular stamps. A poly(dimethylsiloxane) (PDMS) layer,
patterned with protruding and recessed elements in a prior step, is exposed to
a solution of alkanethiols; the rubbery stamps are pressed onto a surface for a
15 short time; alkanethiols react with the gold surface when close contact is
obtained; and a pattern of protected and non-protected Au is obtained. This
10 layer is now exposed to another alkanethiol, adsorbing from solution onto the
unprotected gold surface. A patterned layer is obtained. The process is called
microcontact printing (μ CP). It has been established that formation of the
20 patterned structure occurs within a few seconds.

15 The patterned layer may now be used as ultrathin resists in selective wet
etching, or as templates for the control of wetting, dewetting, nucleation and
25 growth or deposition of other materials. Minimal sizes of 35 nm trenches in
Au layers have been obtained with etching techniques.

30 Patterned self-assembled monolayers (SAMs) allow control of the local
hydrophobic/hydrophilic nature of the surface, and therefore act to control
the deposition of materials. Water will condense on the hydrophilic part of
20 the surface; this allows us to deposit materials from water solution onto a
patterned surface in a regular fashion. Likewise, organic polymers may be
deposited onto the hydrophobic surfaces from organic solvents. Both these
35 approaches allow the formation of patterned structures of deposited material.
25 Selective chemical vapour deposition (CVD) processes onto SAMs
controlling the nucleation behaviour is another approach for pattern
formation in ceramics and metals. Proteins and cells can be selectively
40 adsorbed on patterned surfaces.

30 It is easy to pattern non-planar surfaces with this approach, a near
impossibility with photolithography. Capillaries of radius of curvature 50 μ m
45 have been patterned with structures of dimensions down to a few microns.
This enables the construction of more complex structures on patterned and
non-planar surfaces, relieving one of the tyranny of planar photolithography.

50 The microcontact printing is simple, inexpensive and flexible. With bigger
35 structures (>20 μ m) clean room facilities are not necessary. The stamp can be

5 used and reused many times, providing high fidelity reproduction. Because
the master structure is normally used as a template to prepare "negatives" (as
it were), one can form many identical stamps from a single master, and each
10 one of them can be used some hundred times - multiple copying and parallel
5 processing of the structures is therefore possible. The capital cost of
producing the structures is very low. The fabrication of masters of course
requires other lithographical techniques, such as photolithography or electron
15 beam lithography, but the multiplication of stamps gives parallel production
lines. Micromolding is a small twist to classical molding in that a soft and
10 flexible silicone rubber is used, rather than a hard mold. The elasticity and
low surface energy of this mold material allows it to be removed easily from
the prepared structure. Replica-molding (REM) can be obtained down to the
20 30 nm dimensions. Such methods may be used to prepare optical structures as
in gratings, microlenses, Fresnel lenses and similar designs for the diffraction
15 and refraction of light. Microprinting is best obtained with the technique
named micro-transfer molding (μ TM) where a patterned mold is filled with a
liquid prepolymer, excess liquid removed and the mold pressed against a
25 surface, irradiated or heated to polymerize. After the liquid precursor is
converted into a solid, the mold is peeled away. In a slight modification of
20 this technique (micromolding in capillaries, MIMIC) connected structures are
placed in contact with low viscosity liquids, which fill the channels by
capillary action. These liquids may carry nanoparticles, or solutions for
solgel conversion, or polymers in solution. After conversion of the liquid to a
30 solid, the mold is removed. Processing of the resulting structure by
25 photochemistry or thermal treatment is now possible, for instance converting
a precursor to carbon materials. The remaining structure may now be the
functional element - such as an optical waveguide - or a resist to be used to
etch the underlying material. In a slight twist to this method, SAMIM
40 (solvent assisted MIMIC), a solvent is used to modify the sample surface to
be patterned, and the patterned is defined with a micromold in which the
30 structure is defined.

45 The very important aspect of faithful reproduction over large areas and with
low defect density is not yet fully resolved. In a recent report from IBM
Zurich, it is claimed that structures of 1 micrometer pitch were faithfully
35 replicated without defects over areas of 10 cm², using μ CP or MIMIC.

5 Patterning of monolayers of molecules is the most elegant and novel of these
prior art methods, but is limited to transfer of monolayers, subsequently used
10 for etch resists and surface activating elements. Transfer of polymer patterns
is normally done with MIMIC and microcontact printing. In MIMIC a
5 polymer precursor is patterned by filling channels defined by applying a
stamp onto a surface; in microcontact printing a polymer (precursor) fills the
channels turned upside down, in such a way as to form the structure which is
15 then transferred to the surface. Transfer of polymer layers to functionally
modified surfaces has been reported; see L. Yan, W.T.S. Huck, X.M. Zhao,
10 and G.M. Whitesides, Patterning thin films of poly(ethylene imine) on a
reactive SAM using microcontact printing, *Langmuir*, 15(4): 1208-1214
(1999).

20 The patterning of polymers, and in particular conjugated polymers has been
reported (see Z. Huang, P.C. Wang, J. Feng, A.G. MacDiarmid, Y. Xia, and
15 G.M. Whitesides, Selective deposition of films of polypyrrole, polyaniline
and nickel on hydrophobic/hydrophilic patterned surfaces and applications,
25 *Synthetic Metals*, 85(1-3):1375-1376 (1997); and Z.Y. Huang, P.C. Wang,
A.G. MacDiarmid, Y.N. Xia, and G. Whitesides, Selective deposition of
conducting polymers on hydroxyl-terminated surfaces with printed
30 monolayers of alkylsiloxanes as templates, *Langmuir* 13(24):6480-6484
(1997)) using hydrophobic/hydrophilic modification of monomer adhesion. It
may be difficult to deposit high quality polymers from dispersions and
35 solutions with the materials used in these stamps; in particular, the swelling
of a poly(dimethylsiloxane) stamp in chloroform prevents the patterning of
25 many of the luminescent polymers used for electroluminescent polymer
displays where patterning is desired. These polymers are often solvated in
solvents such as chloroform. Likewise, the patterning of water-soluble
40 polymers prohibits the use of some soft lithography techniques, such as
MIMIC (Y. Xia and G. Whitesides, *Soft lithography*, *Angewandte Chemie-*
30 *International Edition in English* 37(5): 551-575 (1998) and Y. Xia and G.
Whitesides, *Soft lithography*, *Annual Review of Materials Science*, 28:153-
45 184 (1998)) as the solvent is required to pass through an elastomeric
membrane. Chloroform will swell the stamp, and destroy the fine pattern to
be transferred; in the other extreme, water is not easily transported through
35 the extremely non-polar elastomeric stamp, and pattern transfer will be
prohibited. Novel patterning methods are therefore desired.

5 In regard of certain drawbacks and limitations of the above-mentioned prior art methods, it is thus an object of the present invention to provide methods whereby patterns can be generated in thin films of polymer deposited on
10 material surface by a simple and inexpensive technique based on the use of a specially designed stamp for generating the patterns. Particularly it is another
15 object of the present invention to be able to pattern thin film of polymers which initially form continuous layers and moreover exhibit advantageous electronic or optical properties, e.g. for use as pattern electrodes or pixels in optoelectronic displays.

10 Finally, it is also an object of the invention to provide patterned thin films of polymer on a substrate in order to facilitate specific processing of the
20 substrate.

25 The above-mentioned objects and advantages are realized with a method for patterning a polymer film according to the invention the method being characterized by depositing onto the material surface a thin film of polymer,
30 applying to the material surface the stamp made of an elastomeric material in conformal contact with the surface of the thin film, such that portions thereof contacting one or more protruding elements of the elastomeric stamp, the
20 formed by the at least one indentation thereof, are attached to the protruding element or elements and removed from the material surface with the stamp.

35 According to the invention the polymer can advantageously be modified by incorporating additives in order to reduce the cohesive binding of the polymer film, in which case an additive can be a water-soluble organic compound, or selected among ethylene glycol, poly(ethylene glycol),
25 glycerol, sorbitol, polyol, or any combinations thereof.

40 According to the invention the polymer can be a water-soluble or dispersed polymer, or a conducting conjugated polymer in its doped or undoped state, or poly(3,4-dioxyethylenethiophene) (PEDOT) or deriving from a copolymer thereof, or one or more mixtures incorporating the monomer (EDOT) form.

45 30 According to the invention it is advantageous modifying the material surface in order to provide a weak adhesion between the material surface and the polymer film to be removed therefrom, and then preferably modifying the material surface by plasma etching.
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5 According to the invention it is also advantageous modifying the elastomer stamp surface in order to provide a strong adhesion between the stamp and the polymer film to be attached thereto, and then preferably modifying the elastomer stamp surface by plasma etching.

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15 5 Finally it is according to the method of the invention advantageous enhancing the adhesion between stamp and polymer film by means of additives to the latter, an additive then preferably being glycerol.

10 The above-mentioned object and advantages are also realized according to the present invention with a method for transferring a polymer film, the method being characterized by depositing onto the stamp surface a thin film of polymer, applying the stamp made of an elastomeric material in conformal contact with the material surface, such that the thin film of polymer is transferred thereto from one or more protruding elements of the elastomeric stamp formed by the at least one indentation thereof, and leaving a patterned thin film of polymer on the material surface when removing the stamp therefrom.

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35 20 In the above method according to the invention it is advantageous modifying the polymer film by incorporating additives in order to reduce the cohesive binding of the polymer film, the additive then preferably being a water-soluble organic compound, or preferably selected an additive among ethylene glycol, poly(ethylene glycol), glycerol, sorbitol, polyol, or any combinations thereof.

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45 25 In the above method according to the invention it is advantageous that the polymer film is a water-soluble or dispersed polymer, or that the polymer is a conducting conjugated polymer in its doped or undoped state, or poly(3,4-dioxyethylenethiophene) (PEDOT) or deriving from a copolymer thereof, or one or more mixtures incorporating the monomer (EDOT).

45
50 30 In the above method according to the invention it is advantageous modifying the elastomer stamp surface in order to provide a weak adhesion between the elastomer surface and the polymer film to be removed therefrom, and then preferably modifying the elastomer stamp surface by plasma etching.

55 In the above method according to the invention it is advantageous modifying the material surface in order to provide a strong adhesion between the

5 material surface and the polymer film to be transferred thereto, and then preferably modifying the material surface by plasma etching.

10 Finally the above mentioned objects and advantages are provided with the use of the method for patterning or the method for transferring to provide a
5 patterned etch resist in the form of a thin film of polymer on a gold layer, whereby the gold layer can be removed by etching of the area unprotected by the resist, the polymer preferably being PEDOT.

15 Further features and advantages of the method according to the invention are apparent from the appended dependent claims.

10 20 The invention shall now be described in a general manner and in connection with the appended drawing figures in case of one of the methods, as well as with a reference to exemplary embodiments of both the methods.

In the drawing figures,

25 fig. 1 shows the deposition of a thin film of polymer on a substrate,

15 fig. 2 the application of a stamp to the thin film polymer, and

fig. 3 schematically the patterning of the thin film of the polymer.

30 A particular polymer of great interest in these devices is the poly(3,4-dioxoethylenethiophene) (PEDOT) which is a commercial polymer from Bayer AG. It is produced in the form of an aqueous dispersion, and can
35 20 be coated, e.g. spin-coated onto a surface to form a thin film. This film has very attractive properties for polymer electronic devices as it for instance enhances the stability and efficiency of polymer light emitting diodes, or the hole collection in polymer photodiodes, or the hole injection in
40 25 metal/PEDOT/polymer structures. It is, however, difficult to pattern this polymer dispersion with the hydrophobic polydimethylsiloxane (PDMS) stamp in the MIMIC method. Thus the present invention provides alternative methods of patterning PEDOT films.

45 One of the requirements for the use of this patterned film is that sufficient electrical conductivity can be obtained to allow the polymer to be used as the
30 30 electrode in devices. Surprisingly, the patternable film is obtained with similar additives which has been shown to give enhanced electrical conductivity, up to 80 S/cm, after thermal curing.

5 In these methods according to the present invention, a film of modified
PEDOT is deposited on the surface to be patterned by spin coating, and
10 patterning is done by removing parts of the film with a suitable elastomer
stamp. This is the first method according to the invention and shall
5 subsequently be termed "Lift-up". In the alternative method, a modified
PEDOT layer is deposited on the stamp and then transferred onto the surface
to be patterned. This is the second method according to the invention and
15 subsequently termed "Put-down".

20 These methods are superior to prior art in that they allow patterning of very
large areas on (non-planar) surfaces. It is documented in the literature (see
Y. Xia and G. Whitesides, *Soft lithography*, *Angewandte Chemie-
International Edition in English* 37(5): 551-575 (1998); and Y. Xia and G.
Whitesides, *Soft lithography*, *Annual Review of Materials Science*, 28:153-
184 (1998)) that polymers can be deposited onto surfaces in patterns with
15 MIMIC, in which indentations in a stamp act as channels to allow capillary
filling with some polymer solution or precursor polymer. This requires that
all areas to be filled are connected; an isolated pixel cannot be filled by
capillary action. MIMIC will also require long filling time, as the size of
25 channels is reduced and length increased. It is therefore not suited for reel-to-
reel production. Both the methods according to the invention are in principle
compatible with reel-to-reel production, and also allow the patterning of
isolated structures.

35 They are also superior in that the patterning of the polymer layer does not
(necessarily) require the previous patterning of the surface, as for instance in
25 Z. Huang, P.C. Wang, J. Feng, A.G. MacDiarmid, Y. Xia, and G.M.
Whitesides, *Selective deposition of films of polypyrrole, polyaniline and
nickel on hydrophobic/hydrophilic patterned surfaces and applications*,
40 *Synthetic Metals*, 85(1-3):1375-1376 (1997); and Z.Y. Huang, P.C. Wang,
A.G. MacDiarmid, Y.N. Xia, and G. Whitesides, *Selective deposition of
conducting polymers on hydroxyl-terminated surfaces with printed
monolayers of alkylsiloxanes as templates*, *Langmuir* 13(24):6480-6484
30 (1997), and that polymers, not monomers, are deposited.

45 The preparation of the modified polymer is done in order to tune the cohesive
energy of the film, which has to allow the rupturing of the film in both
50 methods; it is also done to tune adhesion to the substrate and/or stamp. The

5 internal cohesion of the film is modified by adding low molecular species in
the present case, but could in general be any additive giving this function. It
10 is, of course, essential that the additives are in no way detrimental to the
function of the layer, and in the present case the additives are actually
5 beneficial to the function.

When considering the advantages of these methods, we note that Lift-up and
Put-down are complementary in the sense that where the former fails, the
15 latter should work. Poor adhesion of the film to be patterned to the substrate
suggests that Lift-up should be used; poor adhesion to the stamp suggests
10 that Put-down could be used.

In Lift-up, the polymer film transfer between stamp and surface is used to
pick up parts of a PEDOT film from a substrate, by attaching an elastomeric
stamp onto the thin film of PEDOT on a fully covered substrate. The
20 molecular contact between film and stamp breaks up the film, and it can now
be micropatterned to any topology by this method. The PEDOT film will also
15 now be prepared with the help of additives, and after transfer the film is
cured/converted to a higher conductivity by thermal treatment. Features of
dimensions down to 10 μm can easily be patterned. One of the advantages of
25 this technique as compared to MIMIC is that isolated PEDOT pixel can be
defined. In this method no solvent is used, which increases the number of
30 materials that can be patterned.

Specifically fig. 1 relates to the lift-up and shows how a PEDOT film is spin
35 deposited on the substrate. In a second step shown in fig. 2 a plasma etched
poly(dimethylsiloxane) stamp is applied to the thin film and simultaneously
25 heated. The stamp may be plasma etched to obtain an adhesion between the
thin film and the stamp which is stronger than the adhesion between the thin
film and the substrate. In the subsequent and final step in the Lift-up process,
40 shown in fig. 3, the stamp is lifted and the thin-film polymer in the form of
PEDOT adheres to the protruding portion of the stamps, such that the pattern
30 is formed in the thin film PEDOT on the substrate when the stamp is
removed.

In Put-down a slightly modified PEDOT dispersion is coated onto an
elastomeric stamp by spin coating. By adding a low molecular weight
50 compound such as ethylene glycol, glycerol or sorbitol in the dispersion, the
35 surface remains sticky enough to attach to another surface brought close. For

5 structures with a large enough spacing between the protruding parts this is
sufficient to transfer the PEDOT residing on the upper edge of the structure
onto a mating surface, at the right temperature and pressure. With the use of
10 the Put-down method one may be able to transfer films with structures
5 smaller than 100 μm . This method has the added advantage that no limitation
to the topology is caused from the filling of channels with liquid, such as in
the MIMIC process. There is also the advantage that the surface to be coated
does not need to be planar; actually non-even surfaces can be handled.

15 It shall now be examples of particularly preferred embodiments according to
10 the invention, including both the lift-up and the put-down processes.

20 Example 1: Lift-up

Poly(3,4-dioxymethylenethiophene)-polystyrenesulfonate (PEDOT-PSS)
(Baytron from Bayer AG) is mixed with glycerol to make a 1:2 weight ratio
mixture. The mixture is spin-coated into a thin continuous layer on a glass
15 surface. An elastomer stamp formed in poly(dimethylsiloxane) (Sylgard 184,
Dow Corning) is plasma-treated for 10 to 30 s in an oxygen plasma. The
relief-patterned stamp is brought in conformal contact with the layer, which
is then heated to 50-100° C for 15 to 60 s and subsequently removed with the
removal of the elastomer stamp. – As an alternative to glycerol sorbitol could
20 be used, but apparently sorbitol mixed PEDOT-PSS works poorly if at all
with Lift-up.

35 Example 2: Lift Up

PEDOT-PSS (Baytron from Bayer AG) is mixed with glycerol to make a 1:1
weight ratio mixture. The mixture is spin-coated into a thin continuous layer
25 on a glass surface. An elastomer stamp formed in poly(dimethylsiloxane)
(Sylgard 184, Dow Corning) is plasma-treated for 10 to 30 s in an oxygen
plasma. The relief-patterned stamp is brought in conformal contact with the
layer, which is then heated to 50-100° C for 15 to 60 s and subsequently
removed with the removal of the elastomer stamp.

40 Example 3: Put-down

45 PEDOT-PSS (Baytron from Bayer AG) is mixed with ethylene glycol to
make a 1:1 molar ratio mixture. An elastomer stamp formed in
poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for
10 s in an oxygen plasma. The relief-patterned stamp is dipped into the
50 mixture and dip-coated. It is brought in conformal contact with an ITO

5 surface and part of the layer is deposited from the stamp onto the ITO,
leaving a layer of patterned PEDOT-PSS mixture.

Example 4: Put-down

10 PEDOT-PSS (Baytron from Bayer AG) is mixed with ethylene glycol to
5 make a 1:1 molar ratio mixture. An elastomer stamp formed in
poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for
10 s in an oxygen plasma. The relief-patterned stamp is dip-coated with the
15 mixture. It is brought in conformal contact with an Au surface and part of the
layer is deposited from the stamp onto the Au, leaving a layer of patterned
10 PEDOT-PSS mixture.

Example 5: Put-down

20 PEDOT-PSS (Baytron from Bayer AG) is mixed with glycerol to make a 1:1
molar ratio mixture. An elastomer stamp formed in poly(dimethylsiloxane)
(Sylgard 184, Dow Corning) is plasma-treated for 10 s in an oxygen plasma.
15 The relief-patterned stamp is dip-coated with the mixture. It is brought in
conformal contact with a Cu surface and part of the layer is deposited from
the stamp onto the Cu, leaving a layer of patterned PEDOT-PSS mixture.

Example 6: Put-down

30 PEDOT-PSS (Baytron from Bayer AG) is mixed with glycerol to make a 1:1
20 molar ratio mixture. An elastomer stamp formed in poly(dimethylsiloxane)
(Sylgard 184, Dow Corning) is plasma-treated for 10 s in an oxygen plasma.
The relief-patterned stamp is dip-coated with the mixture. It is brought in
35 conformal contact with a glass surface and part of the layer is deposited from
the stamp onto the glass, leaving a layer of patterned PEDOT-PSS mixture.

25 Example 7: Put-down

40 PEDOT-PSS (Baytron from Bayer AG) is mixed with glycerol to make a 1:1
molar ratio mixture. An elastomer stamp formed in poly(dimethylsiloxane)
(Sylgard 184, Dow Corning) is plasma-treated for 10 s in an oxygen plasma.
The relief-patterned stamp is dip-coated with the mixture. It is brought in
30 conformal contact with an Au surface and part of the layer is deposited from
the stamp onto the Au, leaving a layer of patterned PEDOT-PSS mixture. The
45 decorated Au surface is exposed to an etchant (gold etch solution: 5g I₂, 10 g
KI dissolved in 250 ml H₂O) to remove the unprotected Au layer.

Claims

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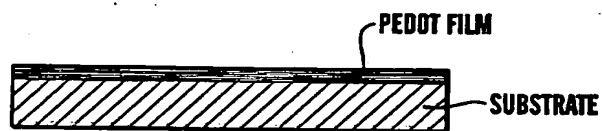
PATENT CLAIMS

1. A method for patterning a polymer film forming a coating on a material surface, wherein the patterning takes place by means of a stamp having a surface with at least one indentation formed therein, characterized by depositing onto the material surface a thin film of polymer, applying to the material surface the stamp made of an elastomeric material in conformal contact with the surface of the thin film, such that portions thereof contacting one or more protruding elements of the elastomeric stamp formed by the at least one indentation thereof are attached to the protruding element or elements and removed from the material surface with the stamp.
2. A method according to claim 1, characterized by modifying the polymer film by incorporating additives in order to reduce the cohesive binding of the polymer film.
3. A method according to claim 2, characterized by an additive being a water-soluble organic compound.
4. A method according to claim 2, characterized by an additive being selected among ethylene glycol, poly(ethylene glycol), glycerol, sorbitol, polyol, or any combinations thereof.
5. A method according to claim 1, characterized by the polymer being a water-soluble or dispersed polymer.
6. A method according to claim 1, characterized by the polymer being a conducting conjugated polymer in its doped or undoped state.
7. A method according to claim 1, characterized by the polymer being poly(3,4-dioxyethylenethiophene) (PEDOT) or deriving from a copolymer thereof or one or more mixtures incorporating the monomer (EDOT) form.
8. A method according to claim 1, characterized by modifying the material surface in order to provide a weak adhesion between the material surface and the polymer film to be removed therefrom.

- 5 9. A method, according to claim 8, characterized by modifying the material surface by plasma etching.
- 10 10. A method according to claim 1, characterized by modifying the
5 elastomer stamp surface in order to provide a strong adhesion between the stamp and the polymer film to be attached thereto.
- 15 11. A method according to claim 9, characterized by modifying the elastomer stamp surface by plasma etching.
- 10 12. A method according to claim 1, characterized by enhancing the adhesion between stamp and the polymer film by means of additives to the latter.
- 20 13. A method according to claim 12, characterized by an additive being glycerol.
- 25 14. A method for transferring a patterned polymer film onto a material surface by means of a stamp having a surface with at least one indentation formed therein, characterized by depositing onto the stamp surface a thin film of polymer, applying the stamp made of an elastomeric material in conformal contact with the material surface, such that the thin film of polymer is transferred thereto from one or more protruding elements of the elastomeric stamp formed by the at least one indentation thereof, and leaving a patterned thin film of polymer on the material surface when removing the stamp therefrom.
- 30 15. A method according to claim 14, characterized by modifying the polymer film by incorporating additives in order to reduce the cohesive binding of the polymer film.
- 35 16. A method according to claim 15, characterized by an additive being a water soluble organic compound.
- 40 17. A method according to claim 15, characterized by an additive being selected among ethylene glycol, poly(ethylene glycol), glycerol, sorbitol, polyol, or any combinations thereof.
- 45 50 55

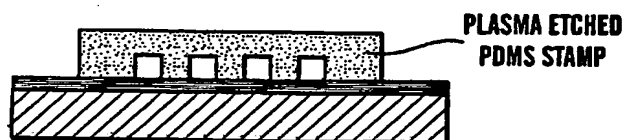
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18. A method according to claim 14, characterized by the polymer being a water-soluble or dispersed polymer.
- 5 19. A method according to claim 14, characterized by the polymer being a conducting conjugated polymer in its doped or undoped state.
- 10 20. A method according to claim 14, characterized by the polymer being poly(3,4-dioxyethylenethiophene) (PEDOT) or deriving from a copolymer thereof or one or more mixtures incorporating the monomer (EDOT).
21. A method according to claim 14, characterized by modifying the elastomer stamp surface in order to provide a weak adhesion between the elastomer surface and the polymer film to be removed therefrom.
- 15 22. A method according to claim 21, characterized by modifying the elastomer stamp surface by plasma etching.
23. A method according to claim 14, characterized by modifying the material surface in order to provide a strong adhesion between the material surface and the polymer film to be transferred thereto.
- 20 24. A method according to claim 23, characterized by modifying the material surface by plasma etching.
- 25 25. The use of a method according to claims 1 or 14 to provide a patterned etch resist in the form of a thin film of polymer on a gold layer, whereby the gold layer can be removed by etching of the area unprotected by the resist, the polymer preferably being PEDOT.

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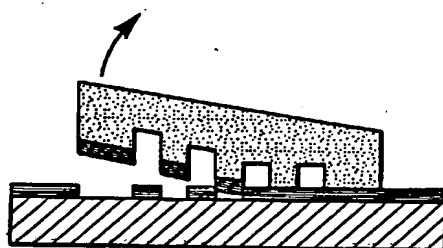
SPIN PEDOT FILM ON SUBSTRATE

Fig. 1



APPLY STAMP AND HEAT

Fig. 2



PEEL OFF STAMP AND STAMP-ADHERED PEDOT

Fig. 3

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 00/00157

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: G03F 7/00, B41M 1/06, B81C 1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: B41M, B81C, G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,OK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

QUESTEL: EDOC, WPIL, JAPIO DIALOG: DIALINDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5512131 A (AMIT KUMAR ET AL), 30 April 1996 (30.04.96), column 5, line 62 - column 6, line 14; column 11, line 22 - line 62, figure 1a	14-16
	--	
A	US 5358604 A (CHARLES W.C. LIN ET AL), 25 October 1994 (25.10.94), column 7, line 11 - column 8, line 9, figures 1-6	14-25
	--	

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"d" document member of the same patent family

Date of the actual completion of the international search

8 August 2000

Date of mailing of the international search report

18-08-2000

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Swedish Patent Office
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INTERNATIONAL SEARCH REPORT

International application No.
NO0000157**Box I** Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).:

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See next page

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO99/00157

I Claims 1-13 describe a method for patterning a polymer film. A stamp is applied to the polymer. Portions of the polymer film are removed with the stamp.

II Claims 14-25 describe a method for transferring a patterned polymer film onto a material surface by means of a stamp.

The "special technical features" in each group of claims are as a whole different from each other. Therefore, these groups of inventions are not so linked together as to form a single inventive concept with regard to PCT Rule 13.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/NO 00/00157

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5512131 A	30/04/96	US 5900160 A	04/05/99
US 5358604 A	25/10/94	NONE	